Theoretical Study of Deprotonation of Polymer Radical Cation for EUV Resist

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Masayuki Endo and Seiichi Tagawa

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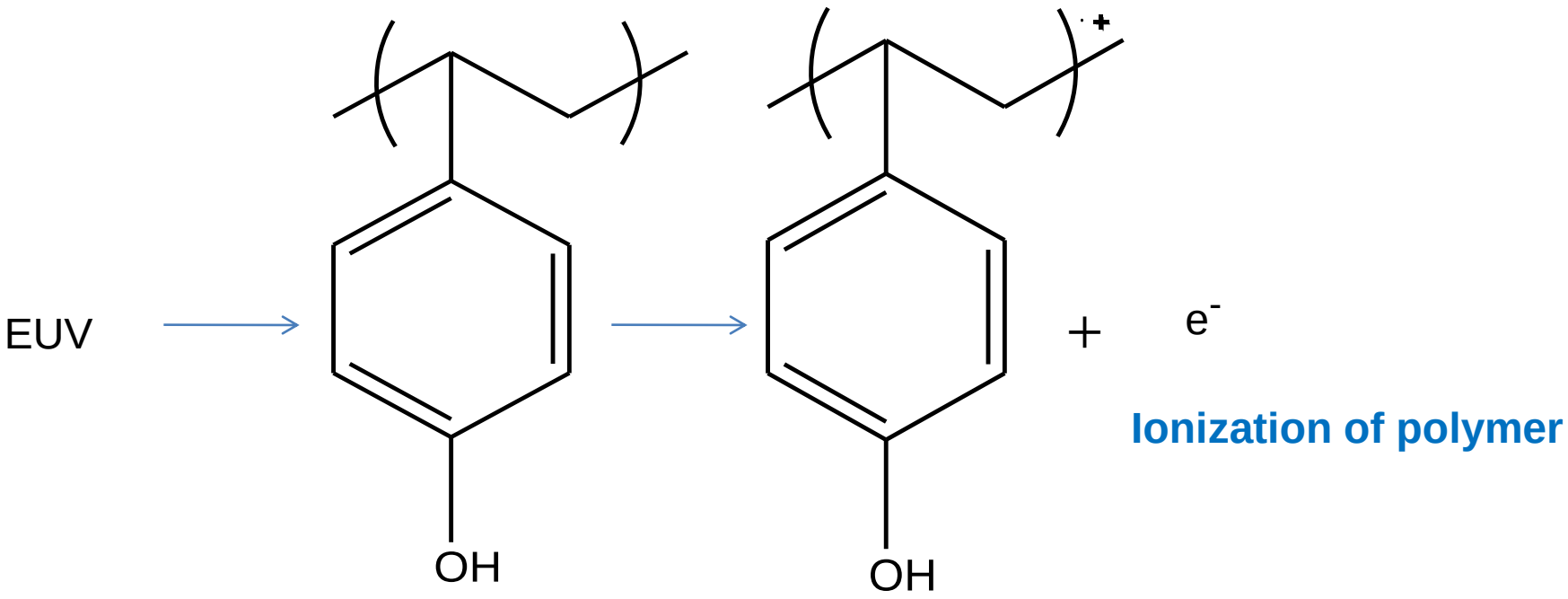
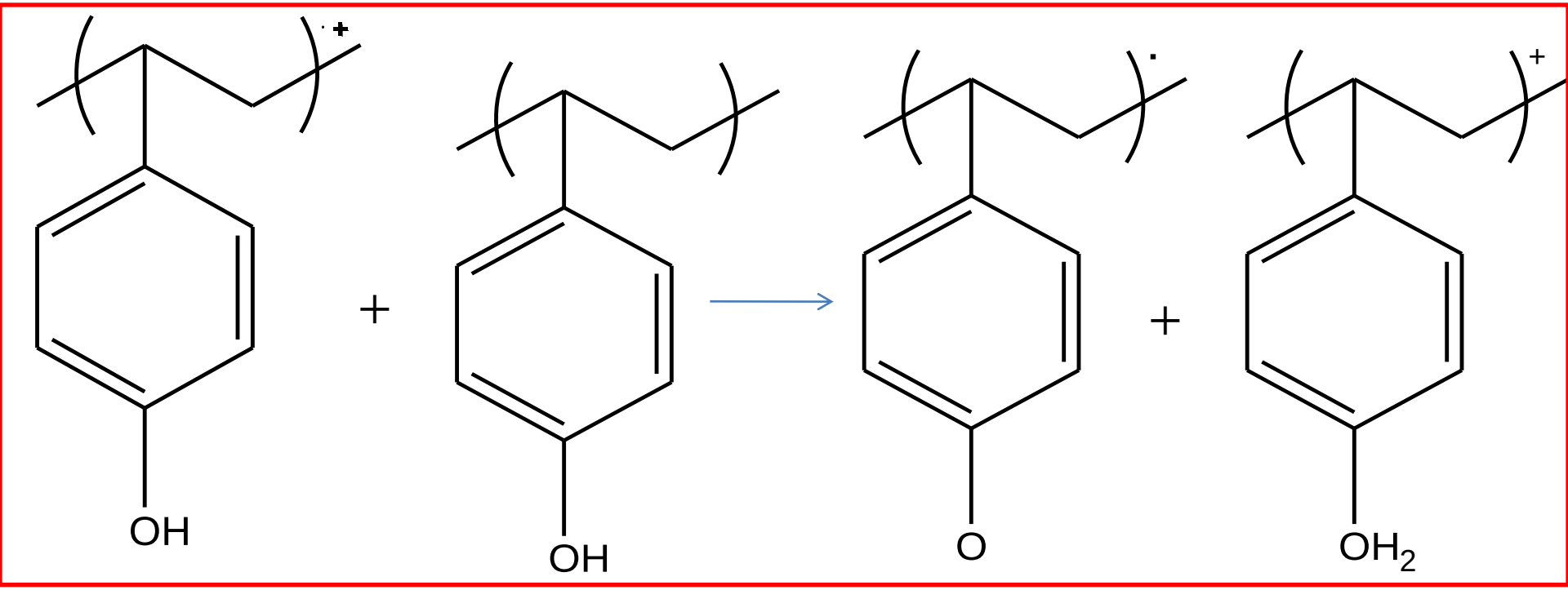
Mechanism of acid generation of EUV resist (1)



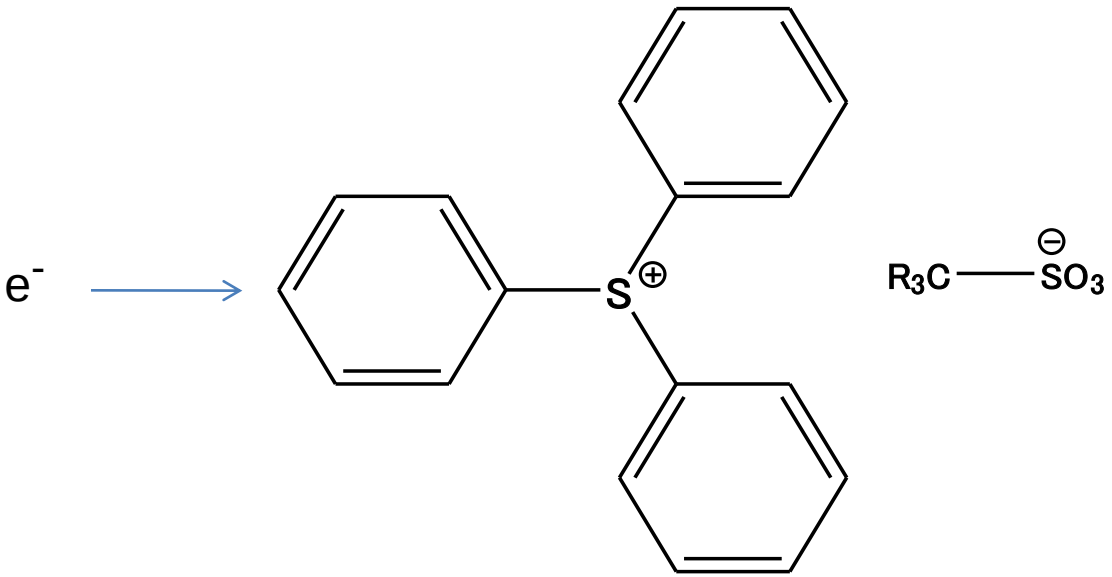
M.Endo and S.Tagawa, J. Photopolym. Sci. Technol., vol.25 (2012) pp.101-108.

Mechanism of acid generation of EUV resist (2)



Deprotonation of polymer radical cation
(This study)

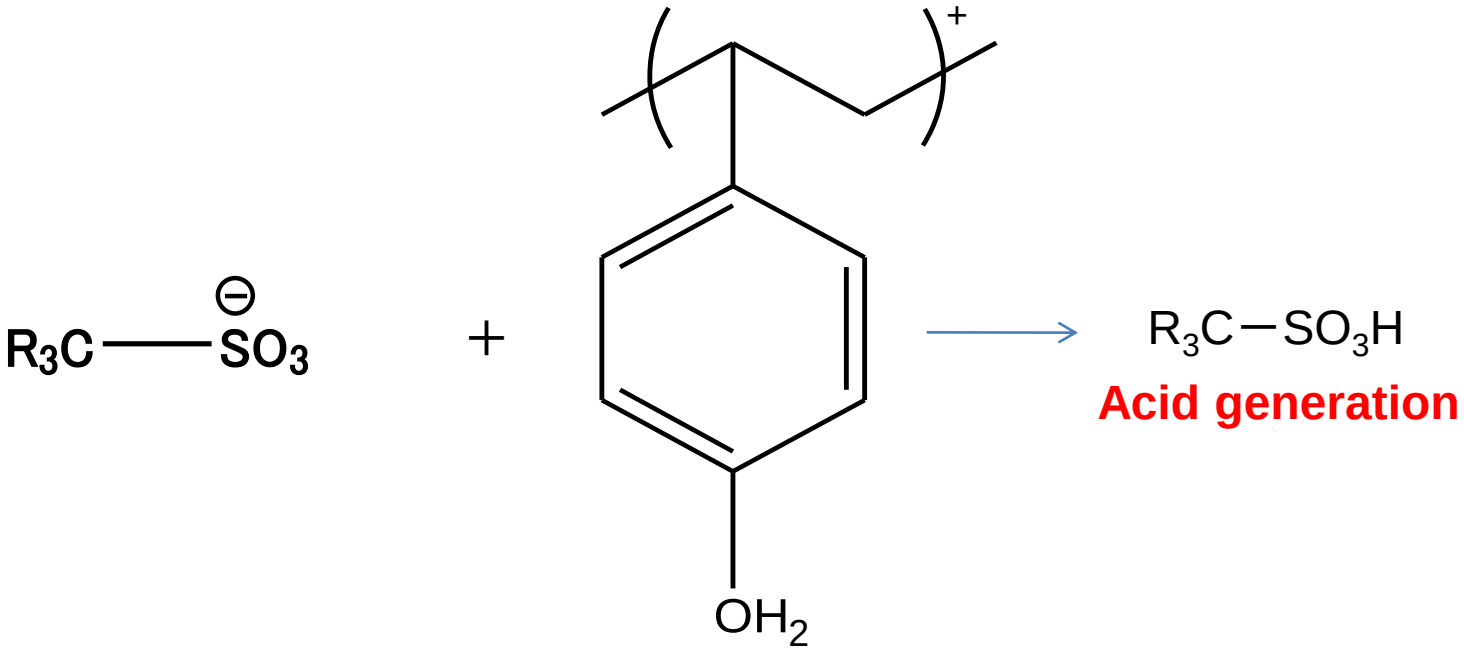
Mechanism of acid generation of EUV resist (3)



Electron affinity of photo acid generator

M.Endo and S.Tagawa, Jpn. J. Appl. Phys., vol.50 (2011) 06GD04.
M.Endo and S.Tagawa, J. Photopolym. Sci. Technol., vol.24 (2011) pp.205-210.

Mechanism of acid generation of EUV resist (4)



Acid generation

Purpose

Investigation of the effects of structures for deprotonation of polymers by theoretical calculation

Energy of optimized molecular structure of polymers (radical, protonation)

− Energy of optimized molecular structure of polymers (radical cation, original polymer)

= Deprotonation energy barrier (Absolute value)

Evaluation of deprotonation as energy barrier

Calculation method

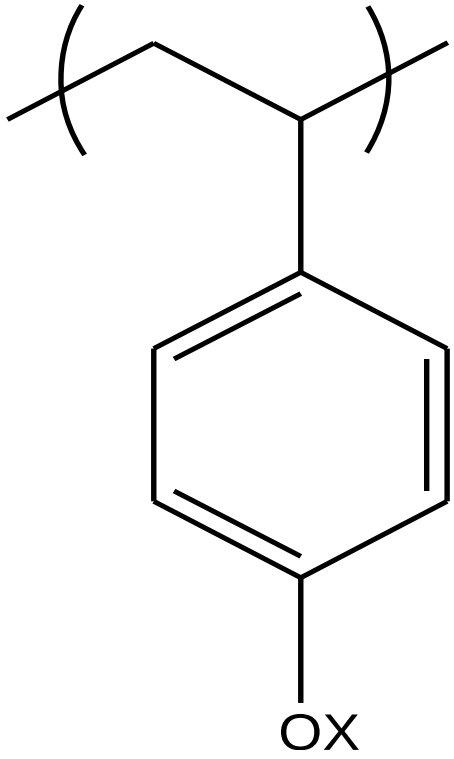
Gaussian09
DFT (Density Functional Theory)
Basis set：6-31G*

○Molecular energy calculation of each polymer by structure optimization
○Molecular orbital analysis
HOMO (Highest Occupied Molecular Orbital)
LUMO (Lowest Unoccupied Molecular Orbital)

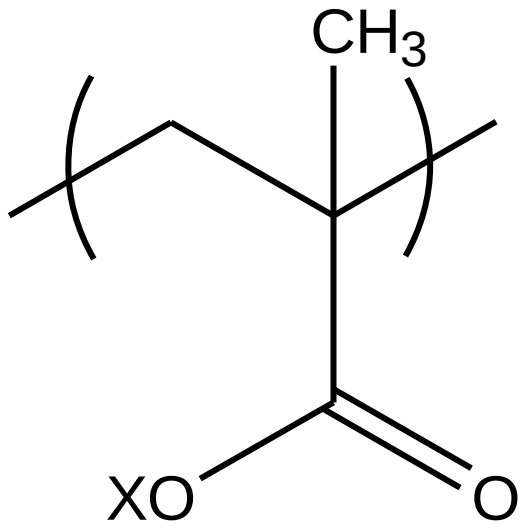
Basis set to present atom precisely
→Reliable results of energy calculation
Relative comparison of energy is possible.

Polymers caluculated

poly(4-substituted oxystyrene)

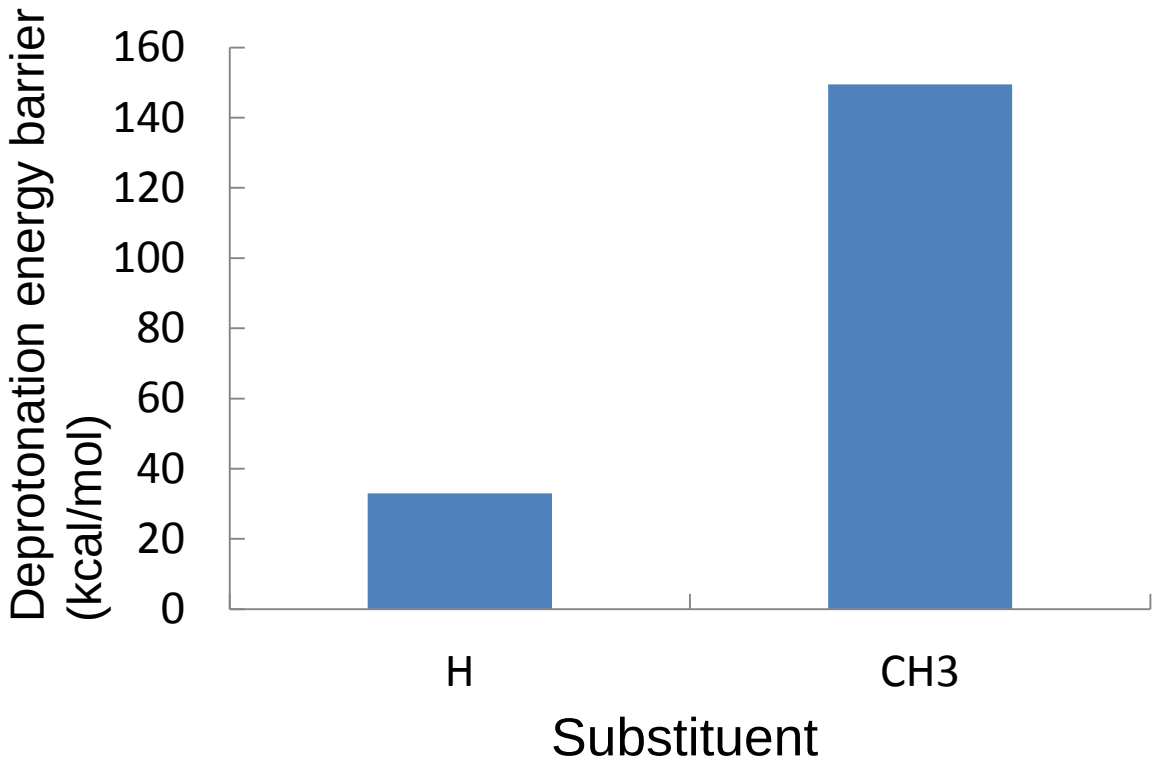


Poly(substituted methacrylate)



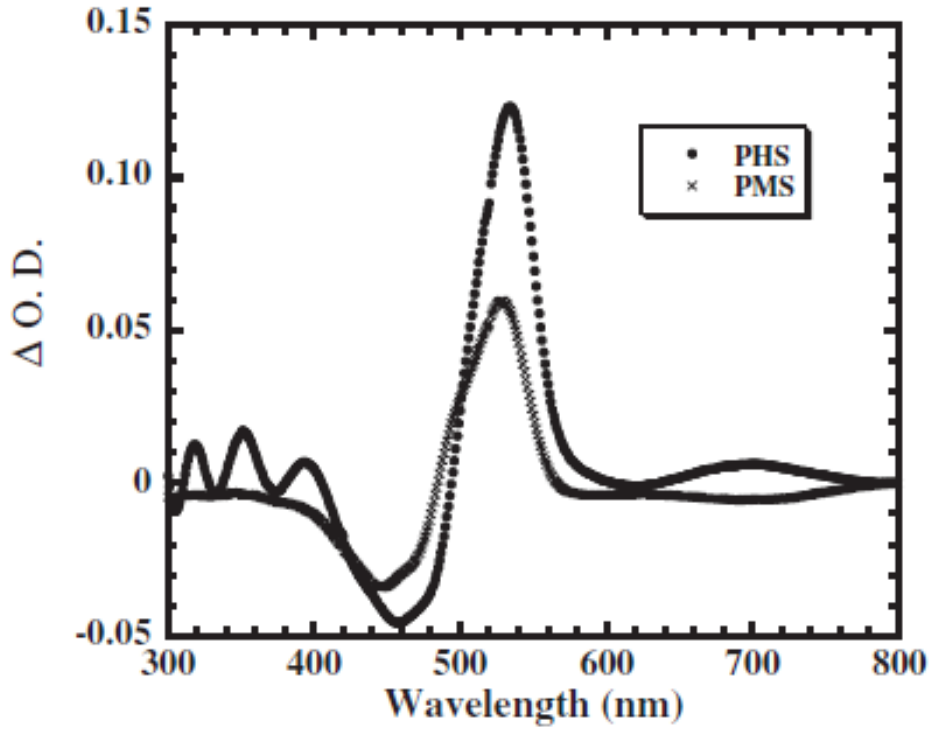
X: substituent

Deprotonation energy barrier: poly(4-substituted oxystyrene)



Deprotonation energy barrier is much smaller for poly(4-hydroxystyrene) than for poly(4-methoxystyrene).

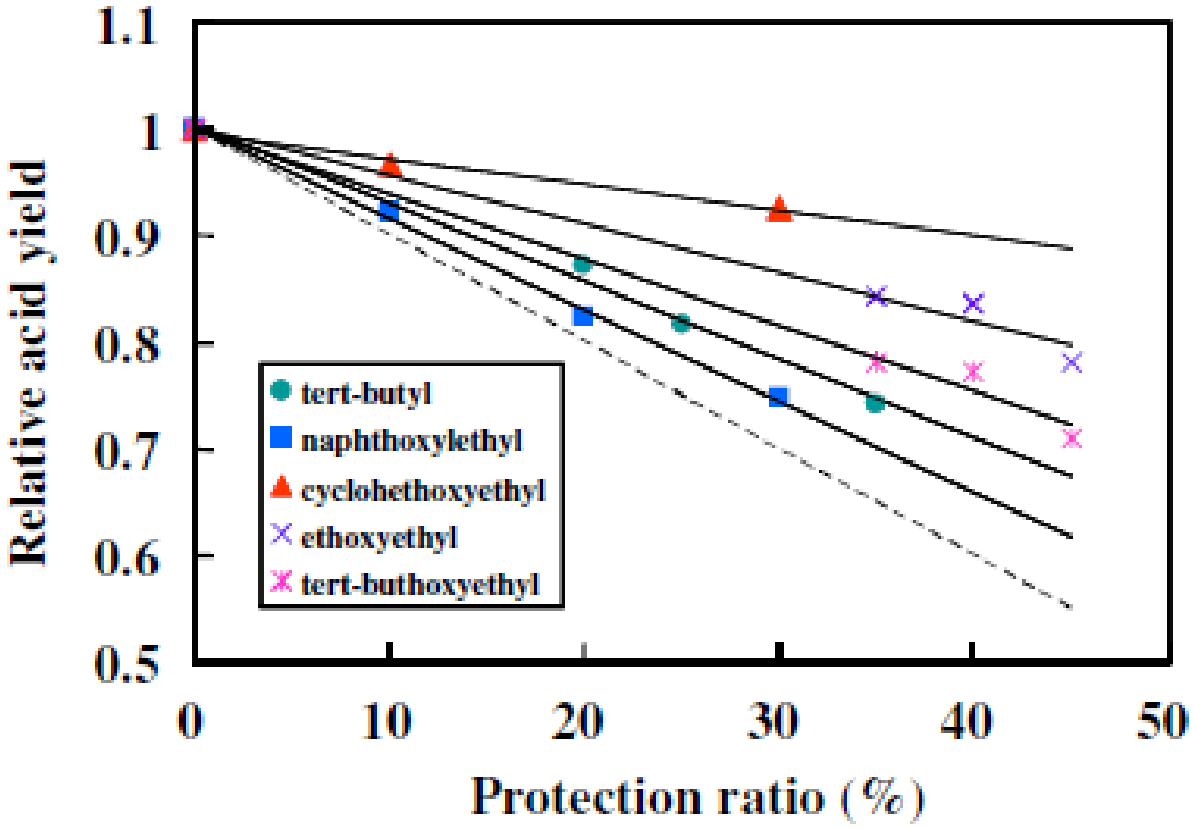
Acid yield in poly(4-hydroxystyrene)(PHS) and poly(4-methoxystyrene)(PMS)



The acid yield in PHS with triphenylsulfonium trifluoromethanesulfonate was about two times higher than that in PMS. This coincides with the tendancy of deprotonation energy barrier.

A.Nakano, T.Kozawa, K.Okamoto, S.Tagawa, T.Kai and T.Shimokawa, Jpn. J. Appl. Phys., vol.45 (2006) pp.6866-6871.

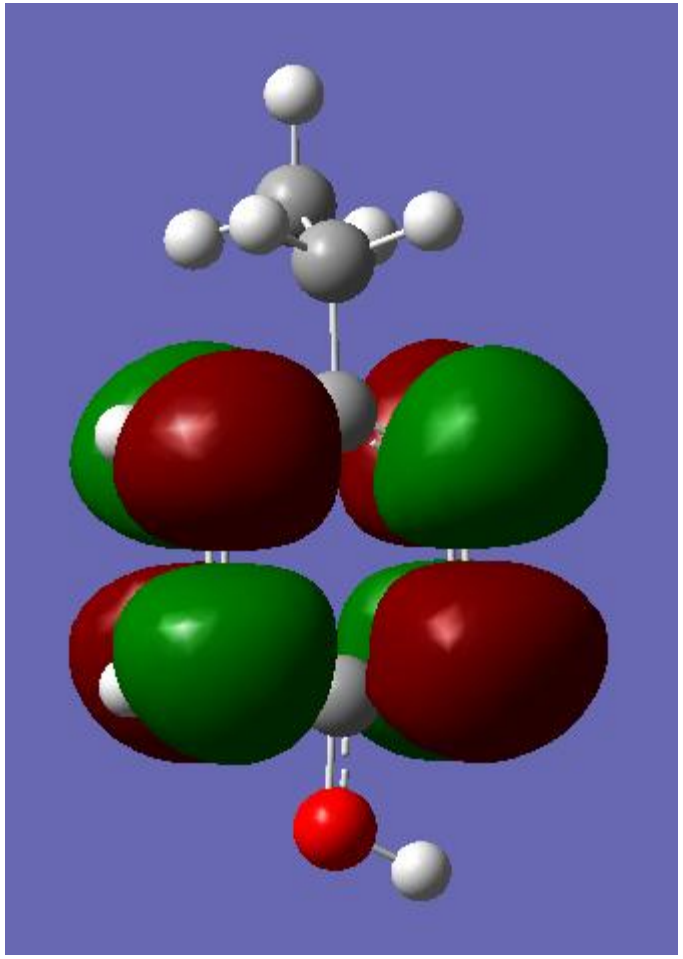
Acid yield of various protection ratios of poly(4-substituted oxystyrene)



More protection ratio, in other words, less hydroxy group decreases the acid yield.

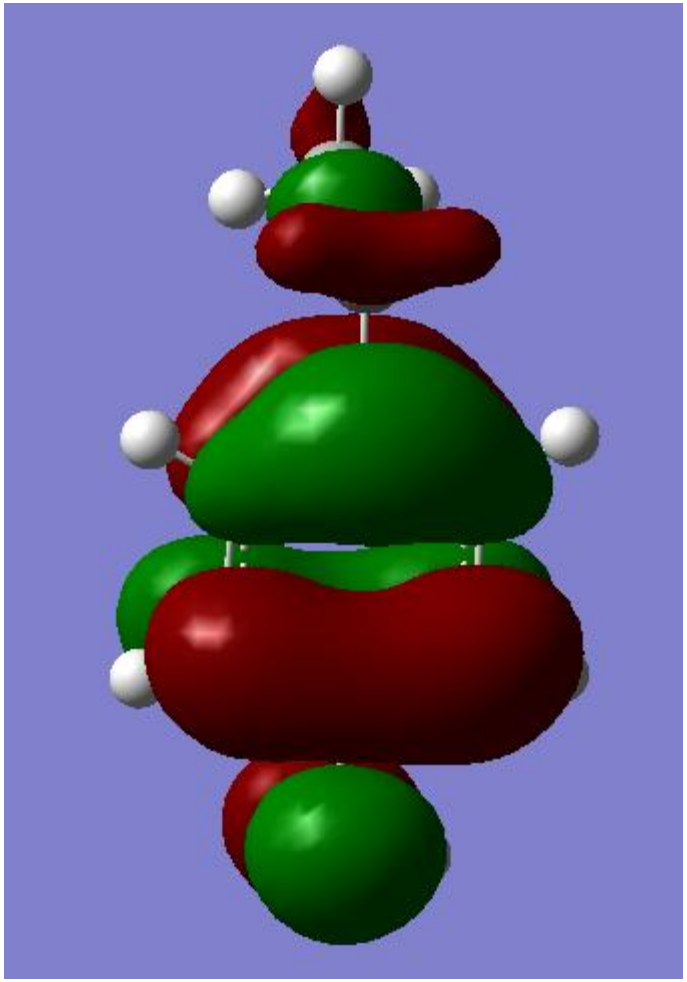
H.Yamamoto, T.Kozawa, A.Nakano, K.Okamoto, S.Tagawa, T.Ando, M.Sato and H.Komano, Jpn. J. Appl. Phys., vol.44 (2005) pp.5836-5838 .

Molecular Orbital: poly(4-hydroxystyrene) before reaction



radical cation

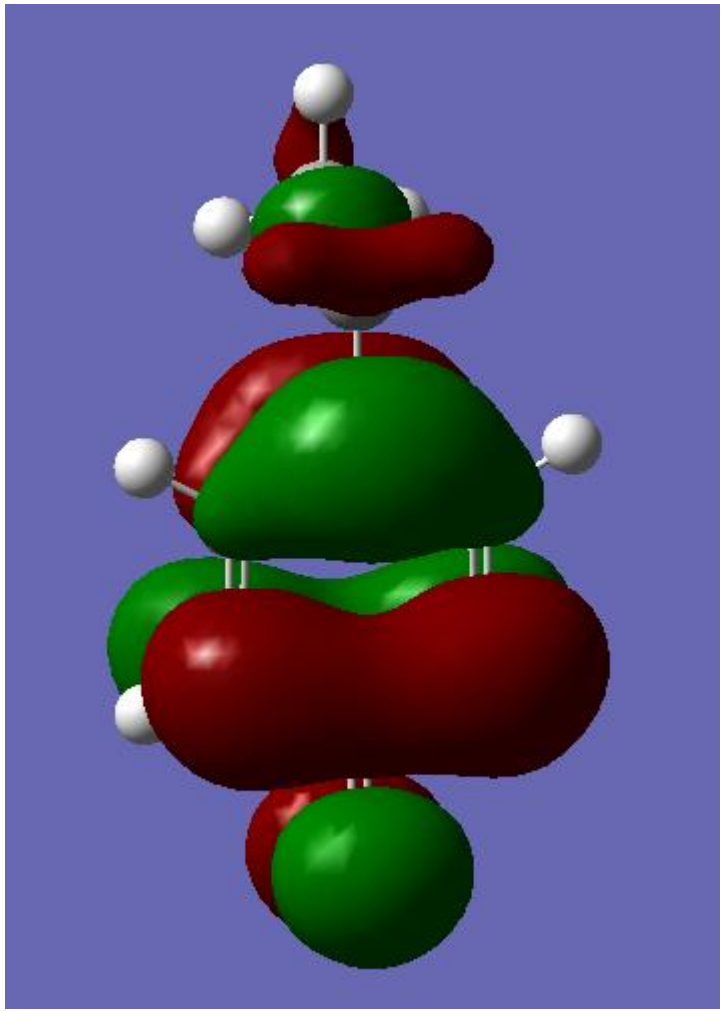
LUMO



original polymer

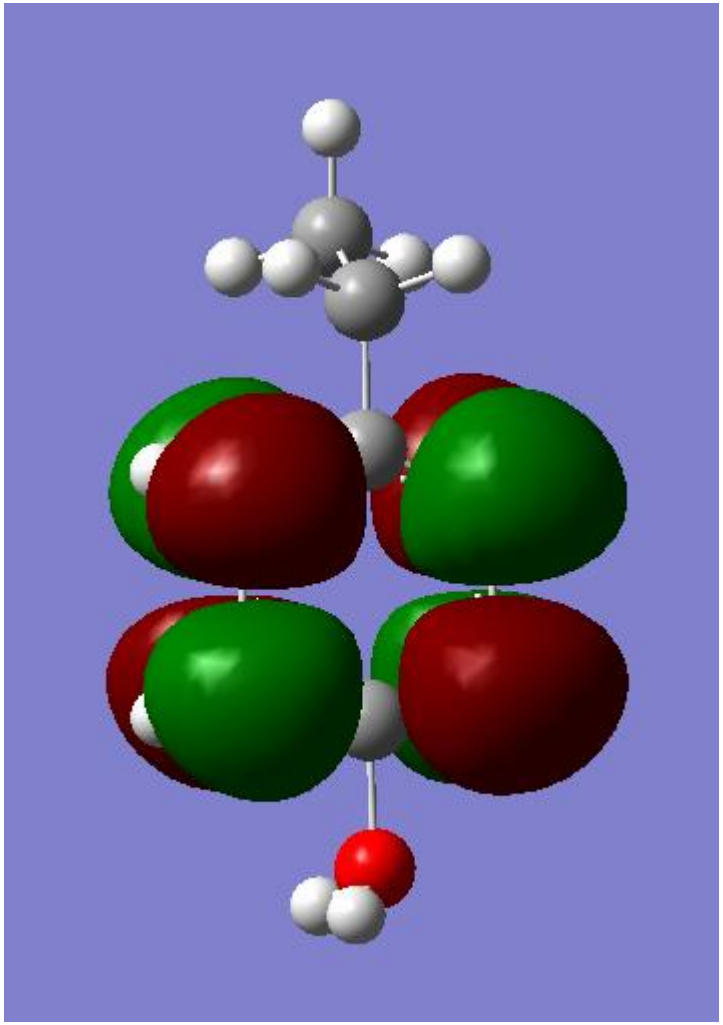
HOMO

Molecular Orbital: poly(4-hydroxystyrene) after reaction



radical

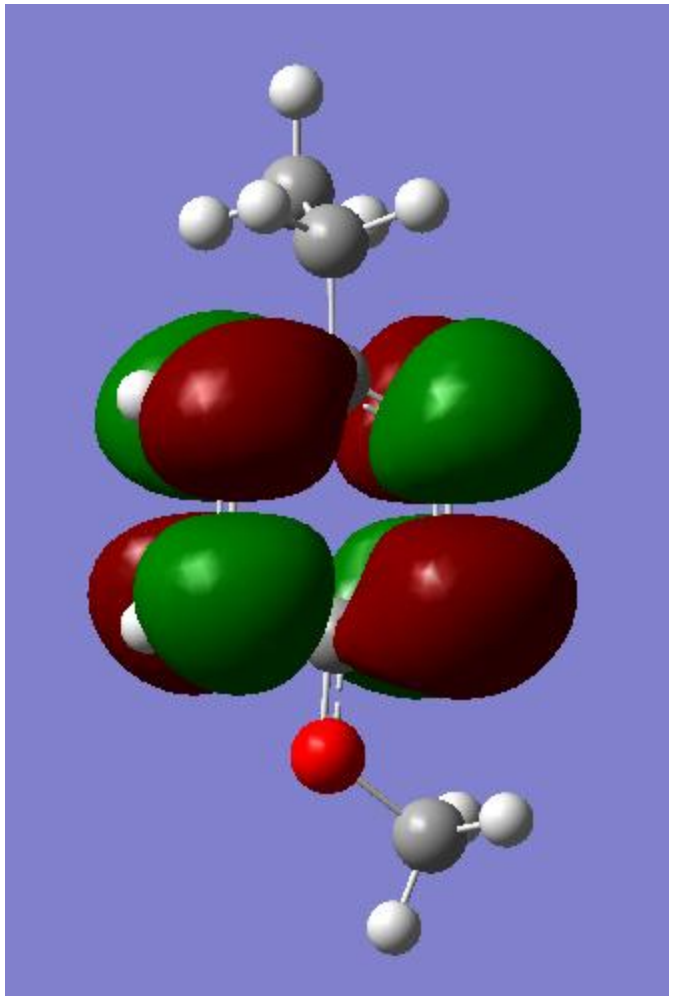
HOMO



protonation

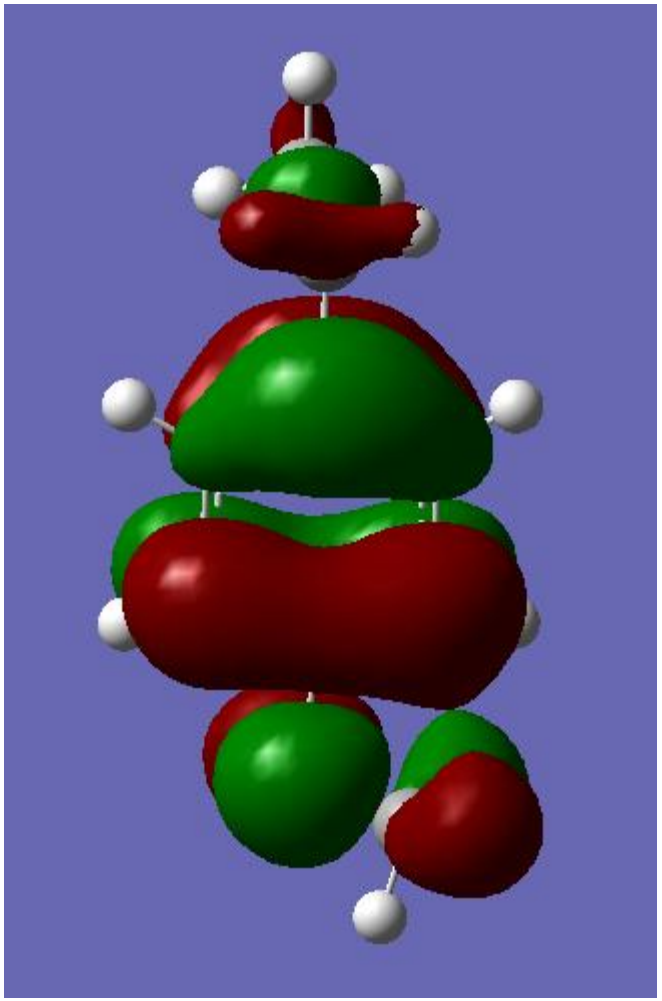
LUMO

Molecular Orbital: poly(4-methoxystyrene) before reaction



radical cation

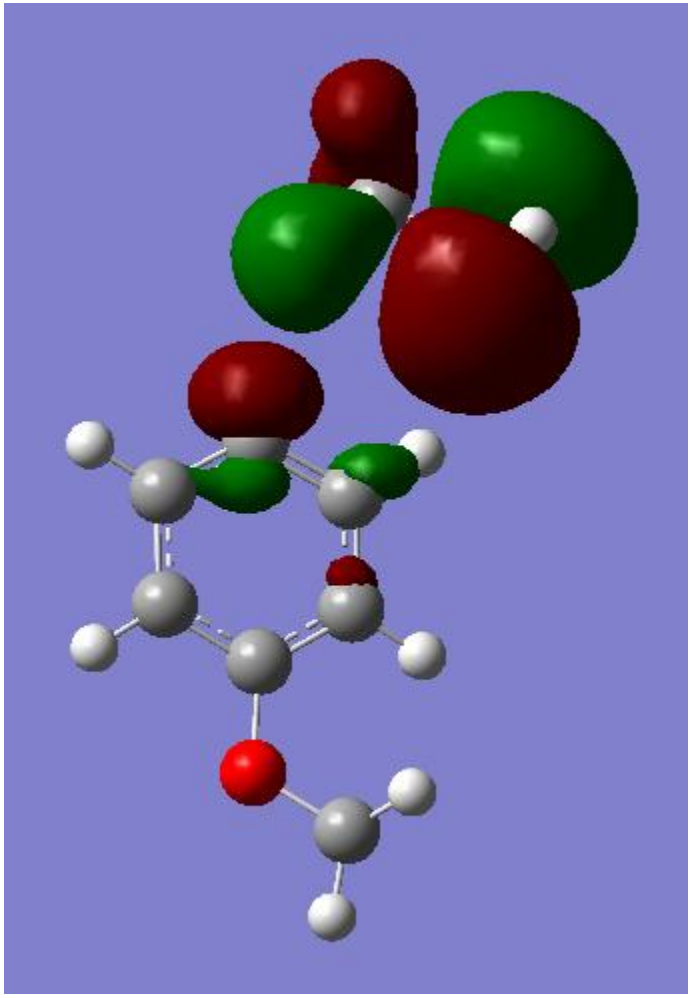
LUMO



original polymer

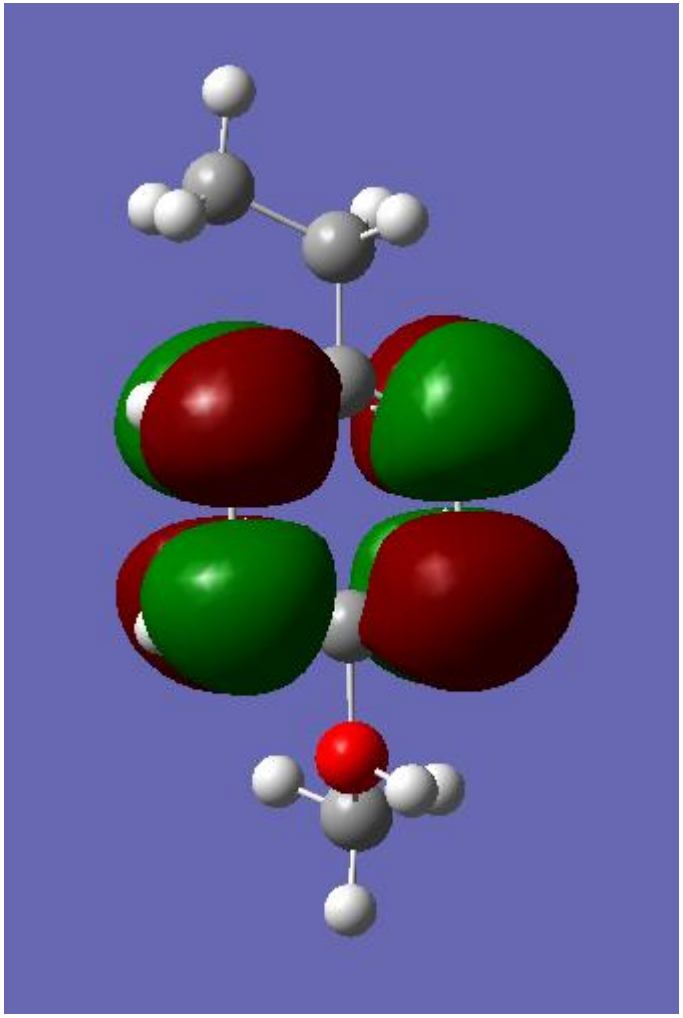
HOMO

Molecular Orbital: poly(4-methoxystyrene) after reaction



radical

HOMO

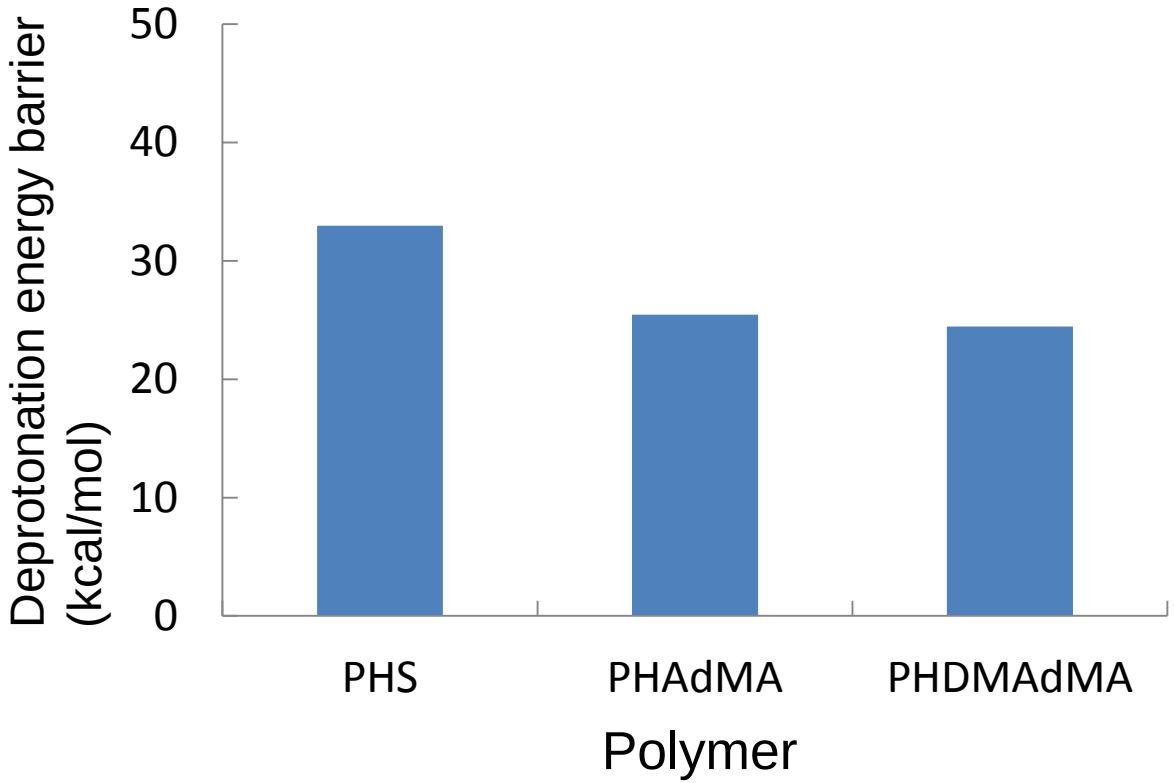


protonation

LUMO

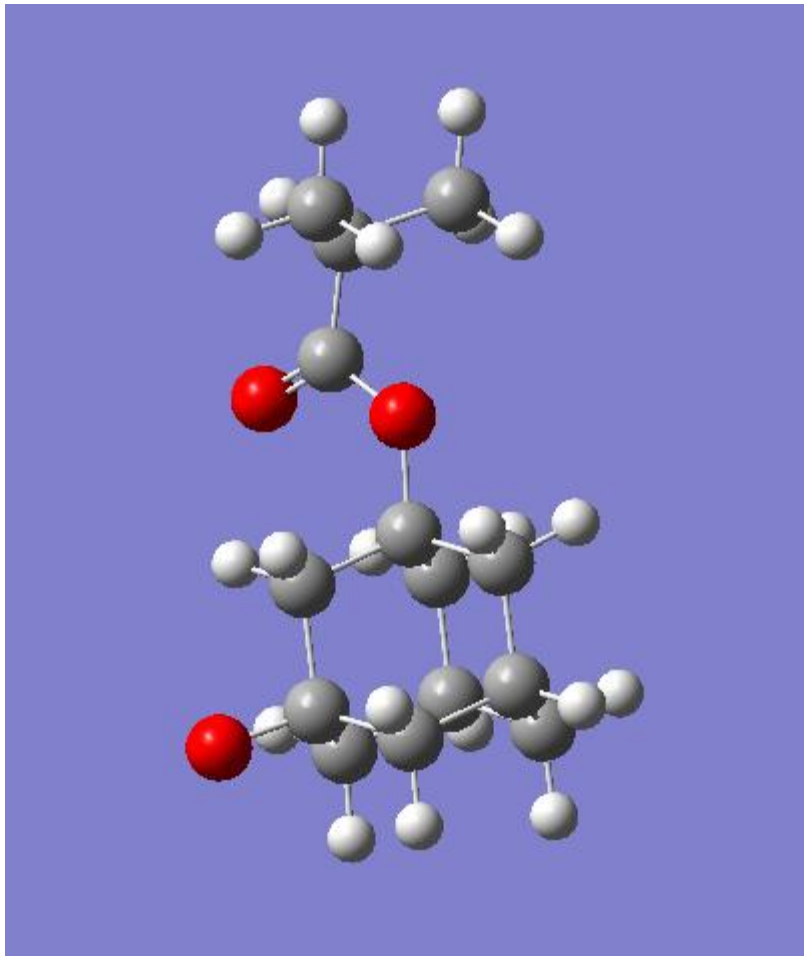
Deprotonation hardly occurs for poly(4-methoxystyrene).

Deprotonation energy barrier:
Poly(4-hydroxy styrene)(PHS),
Poly(3-hydroxyadamantyl methacrylate)(PHAdMA),
Poly(3-hydroxy-5,7-dimethyladamantyl methacrylate)(PHDMAdMA)

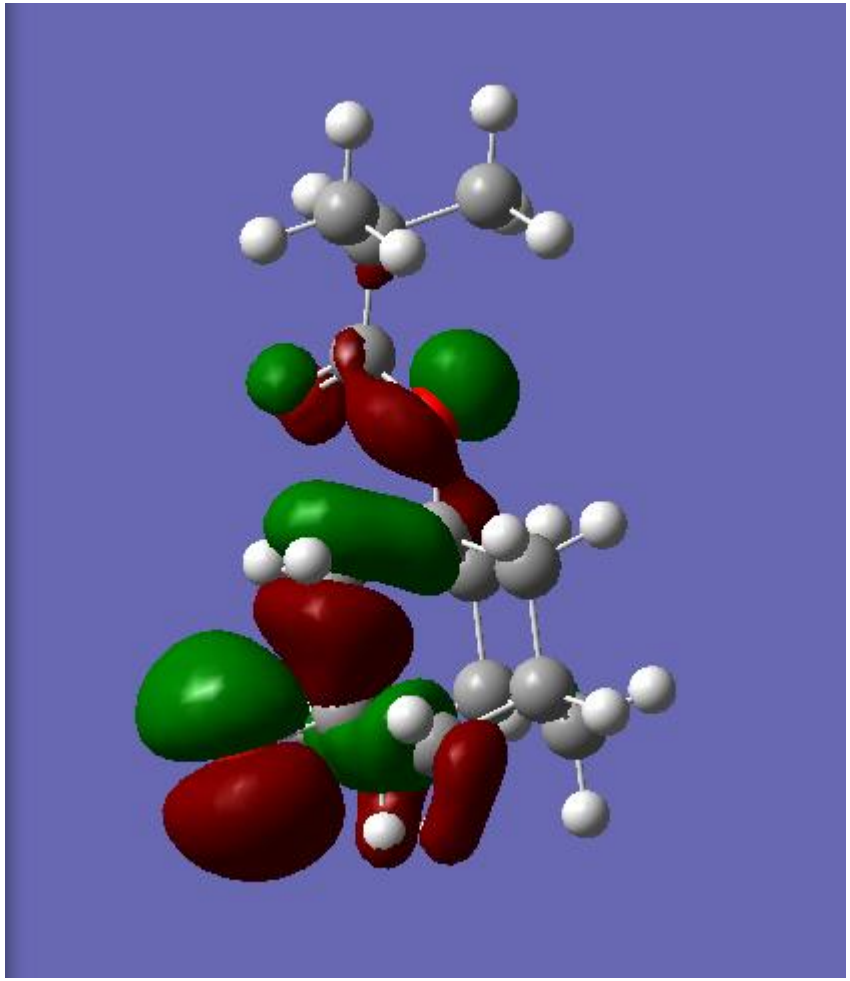


3-Hydroxyadamantyl is effective for the deprotonation of poly(substituted metacrylate).

Molecular model: poly(3-hydroxy-adamantlyl methacrylate)

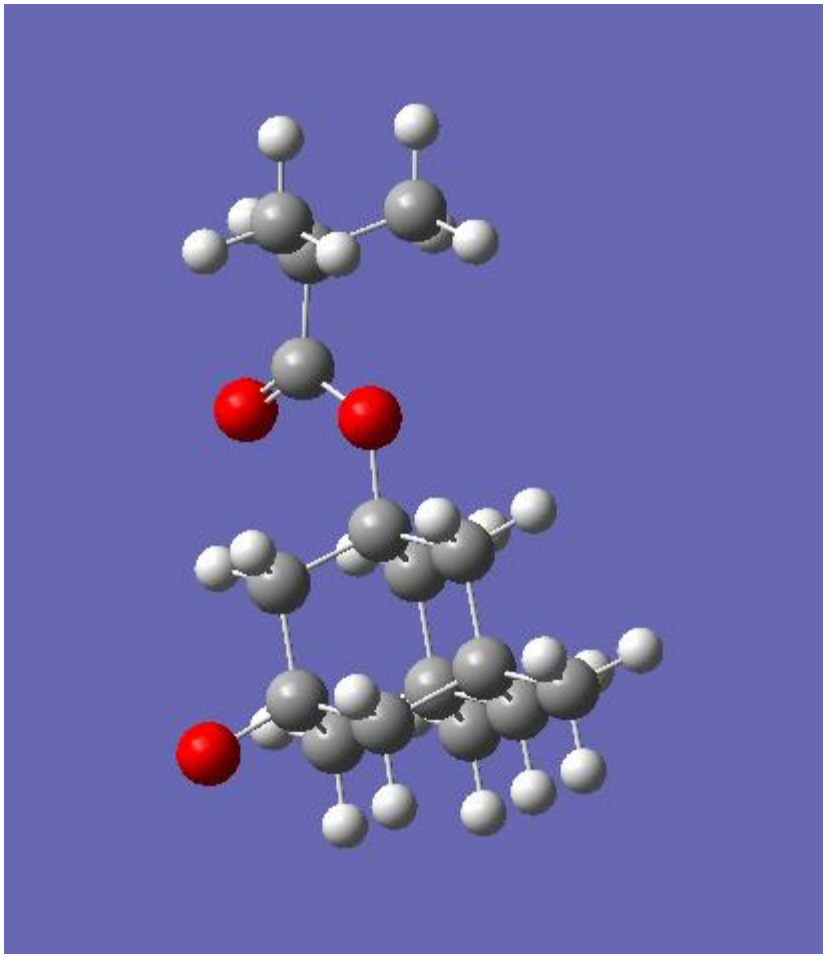


HOMO: radical of poly(3-hydroxy-adamantlyl methacrylate) after reaction

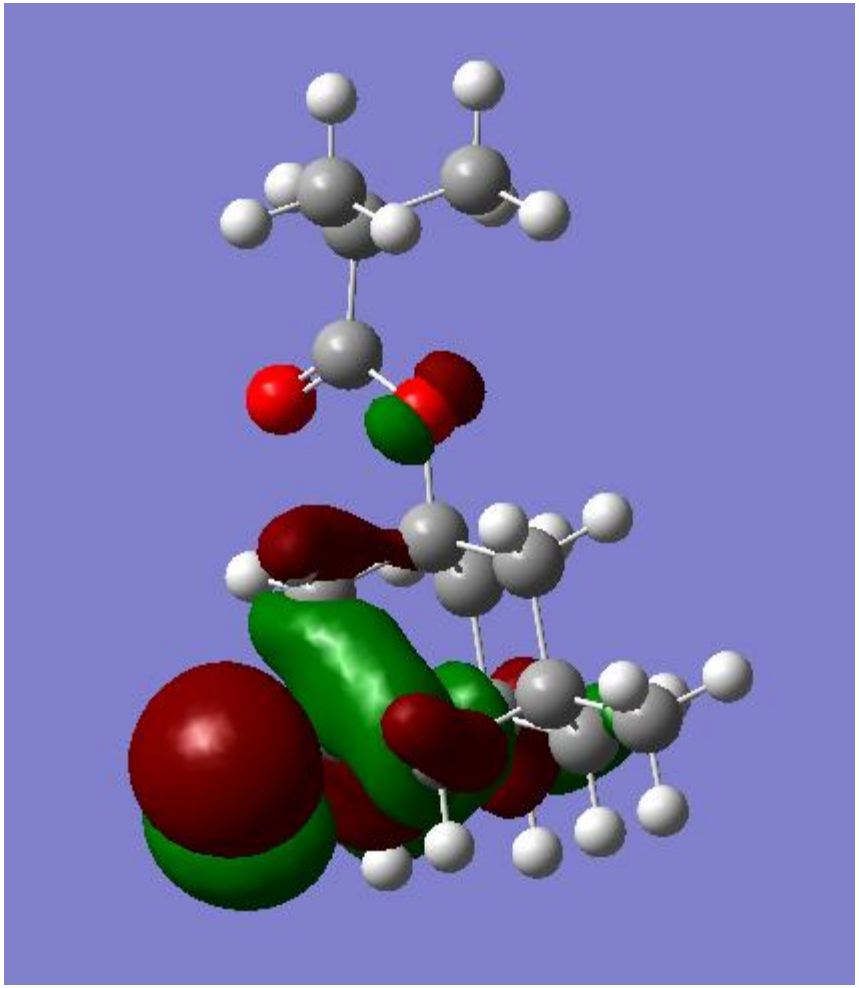


Molecular orbital spreads into hydroxy group, which contributes to the deprotonation.

Molecular model: poly(3-hydroxy-5,7-dimethyl-adamantlyl methacrylate)

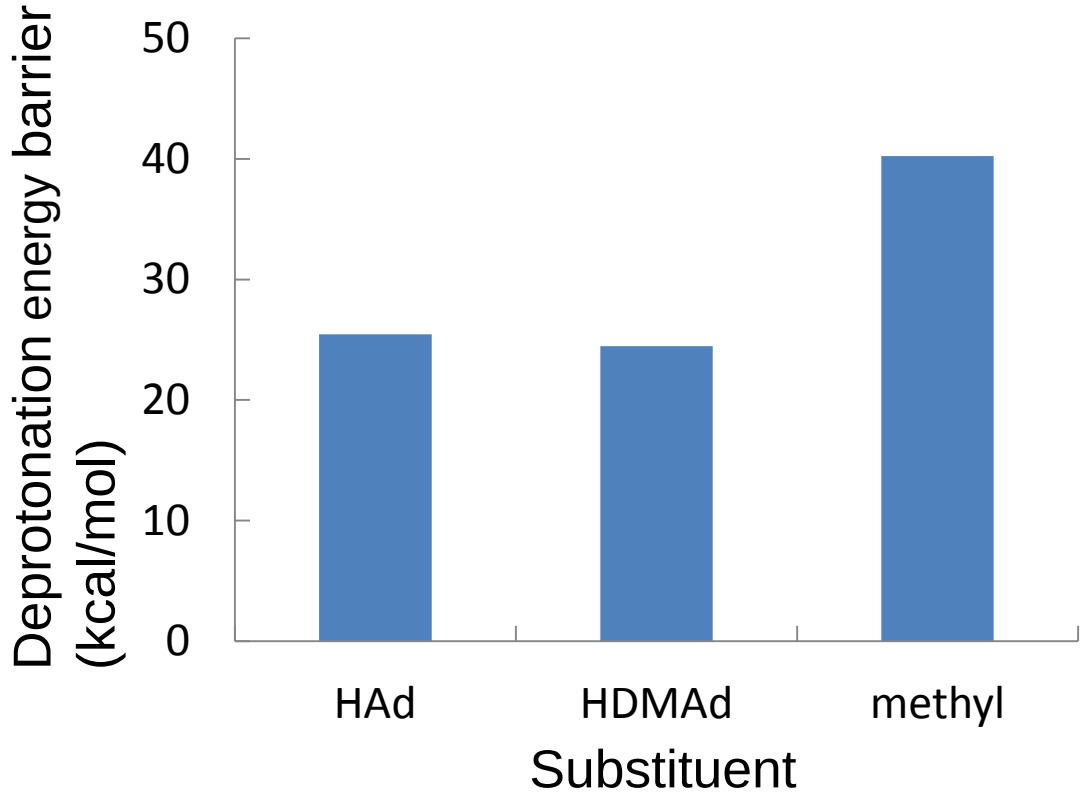


HOMO: radical of poly(3-hydroxy-5,7-dimethyl-adamantlyl methacrylate) after reaction



Molecular orbital spreads into hydroxy group, which contributes to the deprotonation.

Deprotonation energy barrier: Poly(substituted methacrylate): 3-hydroxyadamantyl(HAd), 3-hydroxy-5,7,dimethyladamantyl(HDMAd), methyl



As for the deprotonation, hydroxy group is important for poly(substituted methacrylate).

Summary

The deprotonation of polymer radical cation for EUV resist was evaluated theoretically.

1. **Deprotonation energy barrier is much smaller for poly(4-hydroxystyrene) than for poly(4-methoxystyrene). Phenol group makes more deprotonation and increases the acid yield. Deprotonation hardly occurs for poly(4-methoxystyrene).**

2. **3-Hydroxyadamantyl is effective for the deprotonation of poly(substituted methacrylate).**
   As for the deprotonation, hydroxy group is important for poly(substituted methacrylate). Molecular orbital spreads into hydroxy group, which contributes to the deprotonation.